# Comparative investigation of the coupled-tetrahedra quantum spin systems $Cu_2Te_2O_5X_2$, X=Cl, Br  and $Cu_4Te_5O_{12}Cl_4$

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**Abstract**

We present a comparative study of the coupled-tetrahedra quantum spin systems $Cu_2Te_2O_5X_2$, X=Cl, Br (Cu-2252(X)) and the newly synthesized $Cu_4Te_5O_{12}Cl_4$ (Cu-45124(Cl)) based on *ab initio* Density Functional Theory calculations. The magnetic behavior of Cu-45124(Cl) with a phase transition to an ordered state at a lower critical temperature $T_c$=13.6K than in Cu-2252(Cl) ($T_c$=18K) can be well understood in terms of the modified interaction paths. We identify the relevant structural changes between the two systems and discuss the hypothetical behavior of the not yet synthesized Cu-45124(Br) with an *ab initio* relaxed structure using Car-Parrinello Molecular Dynamics.

*Key words:* spin frustration, density functional theory, quantum antiferromagnets
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Frustrated quantum spin systems have received considerable attention in recent years due to their unconventional behavior. One class of materials belonging to this family are the oxohalogenides $Cu_2Te_2O_5X_2$ (Cu-2252(X)), X=Cl, Br [1] which contain weakly coupled $Cu_4^{2+}$ tetrahedra. These systems show incommensurate long-range ordering at temperatures $T_c$= 18.2 K (Cu-2252(Cl)) and $T_c$=11.4 K (Cu-2252(Br)) [2,3] with strongly reduced ordered moments for the latter system. Evidence for low energy longitudinal magnon excitations have been reported for Cu-2252(Br) [4] and interpreted as a manifestation of the proximity of this system to quantum criticality. An *ab initio* study on the nature of the microscopic interactions performed by us [5] revealed that the knowledge of the subtle ratio between intra-tetrahedra and inter-tetrahedra couplings is crucial for understanding

the behavior of these materials. To shed further light on the physics of this interesting class of materials we add the recently discovered oxohalogenide $Cu_4Te_5O_{12}Cl_4$ (Cu-45124(Cl)) [6] to our considerations and compare it with the previously known Cu-2252.

Magnetic susceptibility experiments performed on the novel Cu-45124(Cl) system show for temperatures below approximately 30 K a different evolution of the antiferromagnetic correlations [6], compared to the Cu-2252 systems. This can be described by a shift of the maximum in the susceptibility from 19 K for Cu-45124(Cl) to 23 K for Cu-2252(Cl) and even to 30 K for Cu-2252(Br). From this shift we derive a smaller averaged magnetic energy scale of the novel system. A kink in the susceptibility marks long range ordering in Cu-45124(Cl) at $T_c$=13.6 K. In the other two com-

pounds the change of slope is weaker and observed at 18.2 and 11.4 K, respectively. Raman scattering experiments show a doublet of sharp excitations with a mean energy $E_m$=36.9 cm$^{-1}$. This energy scale is also reduced compared to the reference systems with $E_m$=47.5 and 60 cm$^{-1}$ for Cu-2252(X) X=Cl and Br respectively. It is noteworthy that the energy of this scattering scales well with the maximum temperature of the susceptibility.

The structural difference between Cu-45124(Cl) [6] and Cu-2252(Cl) [1] is given by an additional TeO$_4$ complex in the middle of the Cu-tetrahedral network in the $ab$ plane, increasing the distance between the Cu$_4$ clusters with respect to Cu-2252(Cl) (see Fig. 1) and the stacking of the Cu$_4$ tetrahedra along the c-axis alternates between successive rows [6]. This results in a centrosymmetric $P4/n$ structure for Cu-45124(Cl) in comparison to the noncentrosymmetric $P\bar{4}$ for Cu-2252(Cl).
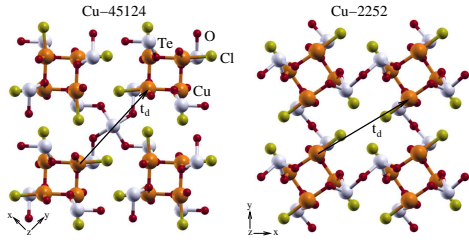


Fig. 1. Crystal structure of Cu-45124(Cl) (left panel) and Cu-2252(Cl) (rigth panel) projected on the $ab$ plane.

We performed *ab initio* DFT calculations and analyzed the resulting electronic structure in terms of the NMTO-downfolding technique [7] in order to investigate the various interaction paths in this system and the relative importance of the intra- to inter-tetrahedral couplings. In Ref. [9] we give a detailed account of the various hopping terms. The most remarkable change observed in this new material is the drastic reduction of the in-plane inter-tetrahedral diagonal interaction $t_d$ (see Fig. 1) which was shown [5] to be mediated by the Cl $p$ orbitals and has been pointed out to play an important role in explaining the magnetic properties [5,8] of the Cu-2252 compounds. This reduction is based on the different alignment of the Cu-Cl bonds belonging to neighboring Cu$_4$ tetrahedra which are parallel to each other in Cu-45124(Cl) instead of pointing to each other as it is the case in Cu-2252(Cl). The resulting Cl$p$-Cl$p$ $\pi$ type bonding in Cu-45124(Cl) is much weaker than the Cl$p$-Cl$p$ $\sigma$ bonding in Cu-2252(Cl). In this sense, this new compound belongs to the limit of very weakly coupled Cu$_4$-tetrahedron systems. This

feature may explain the magnetic ordering at a lower temperature than in the Cu-2252(Cl) system.

In an attempt to predict the behavior of the not yet synthesized Cu-45124(Br) and motivated by the more anomalous properties of Cu-2252(Br) compared to Cu-2252(Cl), we have performed a geometry relaxation for Cu-45124(Br) in the framework of *ab initio* molecular dynamics [10,11] and analyzed the electronic properties with the NMTO-downfolding technique. While the details of these calculations are presented elsewhere [9], we observe that the intra-tetrahedron frustration changes in this system with respect to Cu-45124(Cl) and Cu-2252(Br) while the inter-tetrahedra coupling remains weak. An experimental investigation of this not yet synthesized compound would therefore be highly desirable in the context of frustrated cluster magnetism.

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